This article demonstrates how multinomial processing tree (MPT) models can be used as assessment tools to measure the source of cognitive deficits in clinical populations. The application of this type of modeling is illustrated with a model developed by Batchelder and Riefer (1980, *Psychological Review*) that uses the free recall of category pairs to separately measure storage and retrieval processes in memory. A special version of the model is described that incorporates order constraints in the model's parameters over repeated trails. Computer simulations of the model can be used to address such issues as bias and standard error in the parameter estimates, and how these are affected by individual differences. The article discusses the utility of conducting validity tests of MPT models when used for clinical assessment, and this is illustrated for the pair-clustering model in two experiments. Experiment 1 shows that presentation rate during study affects the storage of clusters but not their retrievability, while Experiment 2 shows that part-list cuing during recall hurts the retrieval of clusters, but does not affect their storage. Experiment 3 and 4 apply the model to two clinical populations: schizophrenics and alcoholics with organic brain damage. The model's analysis reveals that each clinical group suffers deficits in both storage and retrieval compared to a control group. The results suggest that the retrieval deficits are stronger and occur more consistently over trails, whereas storage deficits become significant only on later trails. In addition, the organic alcoholics exhibit no improvement in retrieval over trails, although their storage improves over trails at the same rate as that for the control group.